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Thermochimica Acta 267 (1995) 289–296

thermochimica acta

Thermal diffusivity in a binary mixture of poly(phenylene oxide) and polystyrene[1]

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Received 5 December 1994; accepted 30 January 1995

Abstract

The thermal diffusivity of a binary blend of poly(phenylene oxide) and polystyrene was investigated by the AC Joule heating technique in a practical temperature range including glassy state and melt state. The temperature dependence of the thermal diffusivity and the glass transition temperature (T_g) of the blends were clearly observed. The single T_g, characteristic for this blend, increased with increasing the blend ratio of poly(phenylene oxide). The thermal diffusivity was also dependent on the blend composition.

Keywords: Thermal diffusivity; Poly(phenylene oxide); Polystyrene; Binary mixture

1. Introduction

Thermal diffusivity is a thermophysical parameter which characterizes the rate of temperature diffusion in the material due to a heat flux in the non-steady state heat transfer processes. It is related to the thermal conductivity, λ, according to the formula

$$\lambda = \alpha \cdot C_p \cdot \rho$$

where α is the thermal diffusivity, C_p is the heat capacity at constant pressure, and ρ is the density. Thermal diffusivity is an important transport property both from the theoretical and practical points of view. This characteristic is related to the chemical and physical structure of polymers and is dependent on temperature and pressure. But thermal diffu-

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[1] Presented at the 30th Anniversary Conference of the Japan Society of Calorimetry and Thermal Analysis, Osaka, Japan, 31 October–2 November 1994.

SSDI 0040-6031 (95) 02486-7

sivity has been the less frequently studied thermophysical parameter of polymers [1–7]. Because of the difficulties and the variety of measurement techniques, understanding of the thermal diffusivity of a polymer and its blend system have not yet been established.

Recently we proposed a new simple method for thermal diffusivity measurement [8,9] which was based on the AC Joule heating technique. The temperature dependence of the thermal diffusivities for amorphous and crystalline polymers has been reported. In this study, thermal diffusivity in a binary mixture of poly(phenylene oxide) (PPO) and polystyrene (PS) was investigated. The influence of miscibility on thermal diffusivity was also discussed.

2. Experimental

Polymer specimens in this study, PS and PPO, are commercial polymers. PS was supplied by Sumitomo Chemical Co., Ltd.; $M_w = 22 \times 10^4$. PPO was by Mitsubishi Gas Chemical Company Inc.; $M_w = 3.75 \times 10^4$, $M_n = 1.75 \times 10^4$. PS and PPO were dissolved at 10 wt.% of total polymer in chloroform at each blend ratio. The solution was cast onto a glass plate. After the solvent had been evaporated, the cast film was further dried under a vacuum for 2 days. A clear cast film was obtained for each blend ratio.

A $40\,\mu$m thick cast film of sample was cut into 5–20 mm and inserted between the glass plate, on which gold thin layers 2–20 mm were sputtered. These gold layers, touched with the front and the rear surfaces of the specimens, were used for a heater occurring thermal wave by AC Joule heating and a sensor detecting the temperature wave, respectively. The electrical resistance of the gold layer was controlled at approximately 80 Ohm. Copper lead wires were attached to both faces of each gold layer. Spacers were also inserted between the glass plates to hold the constant thickness of the sample. The scheme for the specimen is shown in Fig. 1a.

Other types of specimens were also prepared for measurement. The gold thin layers were sputtered on both surfaces of the sample directly across an area 1.5–5 mm as shown in Fig. 1b. Copper lead wires were also attached to both faces of each gold layer. To avoid deformation of shrinkage or melting, the samples were mounted between two thin glass plates which were bonded in place by a heat-resistant inorganic adhesive. The frequency of the temperature wave varies twice higher than that of the applied voltage. These thermal waves diffuse across the sample in the vertical direction to the rear surface. The temperature variations on the rear surface are detected by the gold layer sensor as resistance variation which is analyzed using a NF type 5610B lock-in amplifier.

The phase delay of the temperature oscillation at the sensor resistance is obtained by the signal voltage $V(t)$ across the resistance in Fig. 2. $V(t)$ is a function of the temperature oscillation $T(d,t)$, where d is the thickness of the sample and t is time. $T(x,t)$ is derived by solving the one-dimensional heat diffusion equation with the boundary conditions. The relationship between thermal wave frequency and the phase shift of the signal at the rear surface can be expressed by Eq. (1)

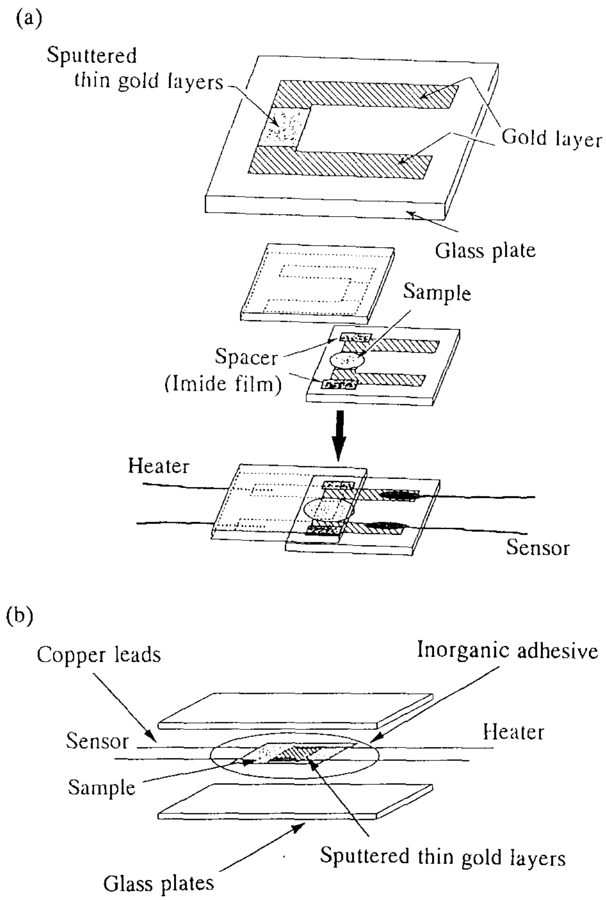

Fig. 1. (a) Models for the sample-heater-sensor geometry with a glass cell. (b) Models for the sample-heater-sensor geometry with adhesives (cited from Ref. [17]).

$$\Delta\theta = \sqrt{(\pi f/\alpha)}\cdot d + \pi/4 \qquad (1)$$

where $\Delta\theta$ is phase shift, α is the thermal diffusivity, f is the frequency of thermal modification, d is the sample thickness. Fig. 2 shows an apparatus for the thermal diffusivity measurement. Since this method is based on the phase shift measurement, the influence of the backing materials can be neglected. The specific heat of polymers were measured by power compensation differential scanning calorimetry (DSC), Perkin Elmer DSC-7. The 10 mg sample enclosed in an aluminum pan was pre-heated at a temperature higher than the glass transition temperature, cooled by 10°C min^{-1} to the room temperature and then heated by 10°C min^{-1} at the atmosphere of herium.

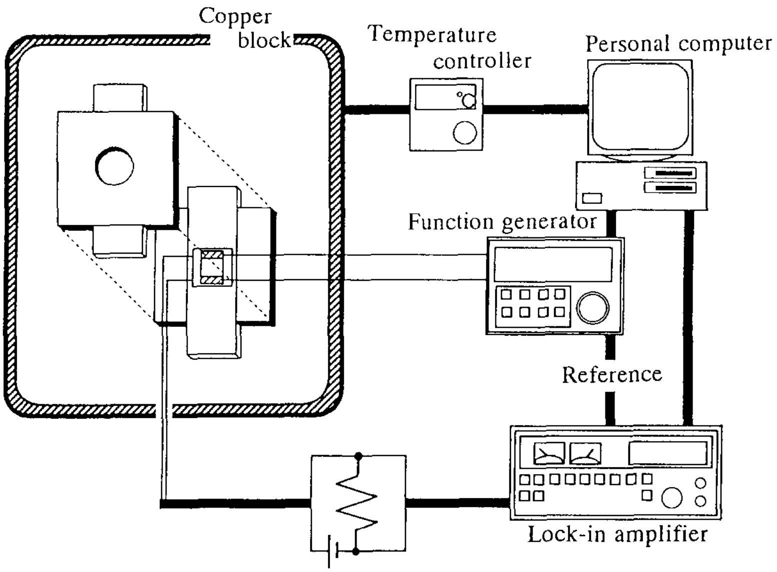

Fig. 2. Apparatus for the measurement system of thermal diffusivity.

3. Results and discussion

Fig. 3 shows typical data on the relationship between the square root of *f* and the phase shift $\Delta\theta$ at the temperatures corresponding to the solid and melt state of PPO/PS blend. It is found that a linear relationship exists between the square root of *f* and the phase shift. The thermal diffusivity can then be obtained from Eq. (1). The thermal dif-

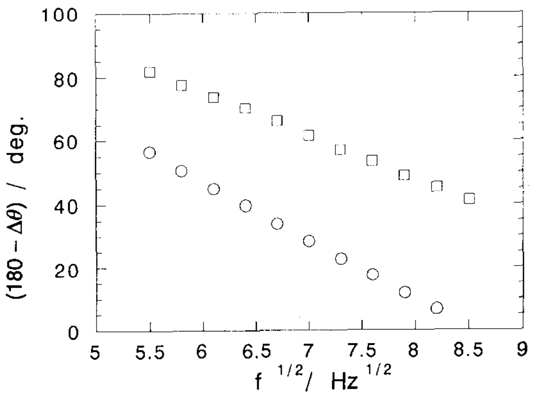

Fig. 3. Phase shift versus the square root of the frequency for the blend of polystyrene (PS) and poly(phenylene oxide) (PPO); 20/80 (wt./wt.); at 50°C (□) and 220°C (○).

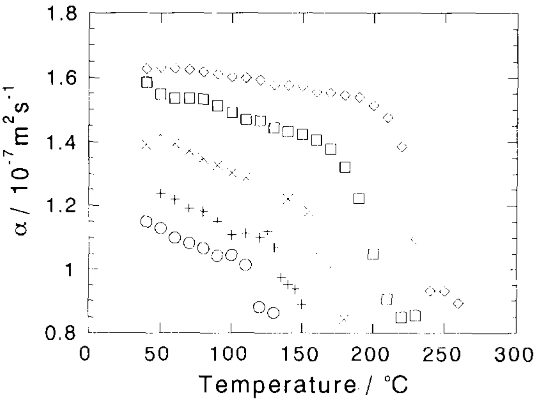

Fig. 4. Temperature dependences of thermal diffusivity α in PS (+), PPO (O), and PS/PPO blends: 80/20, ×; 60/40, ◇ and 20/80, □ (wt./wt.).

fusivity of PS, PPO/PS blends and PPO are shown in Fig. 4 as a function of temperature under cooling runs from the melt state to the solid state. The value increases with decreasing temperature, and a rapid jump up is observed at a temperature corresponding to the glass transition temperature (T_g). A single glass transition was observed in PPO/PS blends at each blend ratio. T_g was determined as the middle point of the temperature during the glass transition. The relation between T_g and the blend composition is shown in Fig. 5. The relation is in good agreement qualitatively with that reported in the literature by other several methods [10–14]. The glass transition temperature increases with increasing the weight fraction of PPO and its change rule is lower than the additivity.

In these blends, the specific heat was also measured by DSC and T_g was determined as the middle point of the transition. The results by DSC are shown in Fig. 5. At the same

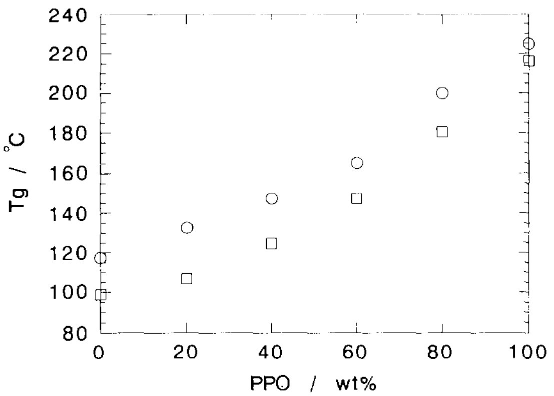

Fig. 5. The glass transition temperatures versus the blend composition; determined by the measurement of the thermal diffusivity (O) and by DSC (□).

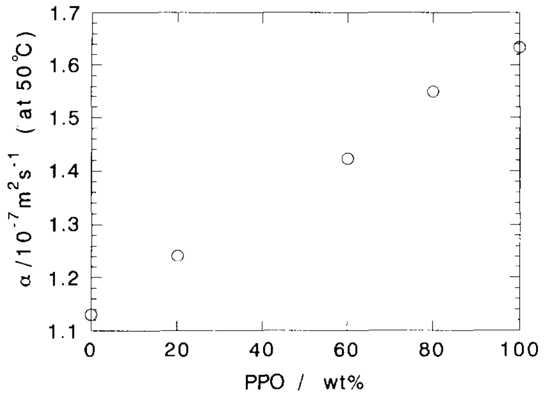

Fig. 6. The change in the thermal diffusivity at 50°C in PS/PPO blends with various weight fractions of PPO.

blend composition the glass transition temperature determined by the thermal diffusivity measurement is higher than that by DSC at 15–20°C. It was considered that the difference in T_g was caused by the difference in frequency of the thermal wave and the scanning rate. At the same temperature, the value of the thermal diffusivity in the blends depends on the blend composition. Fig. 6 shows the variation of the thermal diffusivity at the glassy state (50°C) with the blend composition. The thermal diffusivity of the blend increases with increasing the weight fraction of PPO. The change of the thermal diffusivity in the blends are almost described by the additivity of the thermal diffusivity of PS and PPO corresponding to the blend ratio.

PPO and PS are miscible at all temperatures and the blend composition [10–14], which means two polymers entangled with each other in the order of molecules. In PS/PPO blends, the entanglement density increased with increasing the weight fraction of PPO [15]. The plot of thermal diffusivity and the entanglement density was shown in Fig. 7. It

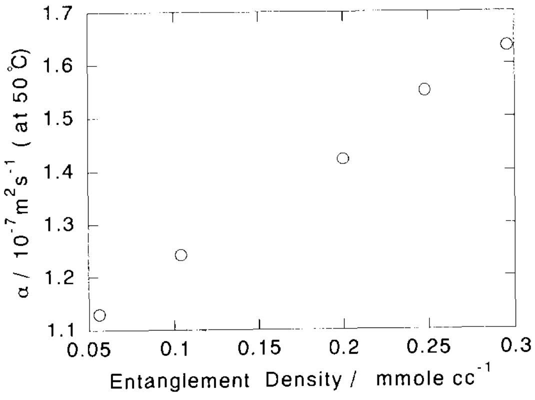

Fig. 7. The relation between the entanglement density and thermal diffusivity at 50°C.

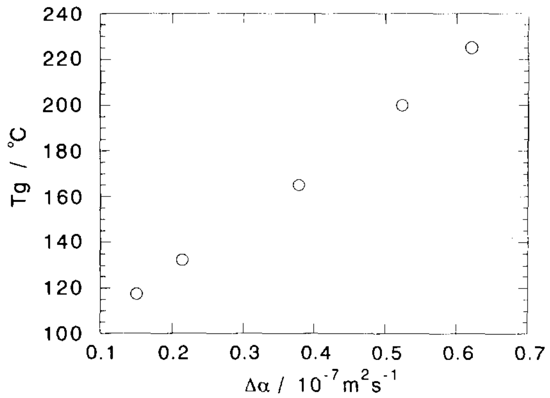

Fig. 8. Glass transition temperature(T_g) of PS/PPO blends plotted against $\Delta\alpha$; the change in thermal diffusivity during the glass transition.

is shown that the thermal diffusivity is related to the molecular parameter for polymers such as entanglement density. During the glass transition the thermal diffusivity and the specific heat changed discontinuously. The relationship between T_g and ΔC_p [16] was investigated for polymers. Fig. 8 shows the relationship between T_g and $\Delta\alpha$ in PPO/PS blends. It was found that T_g increased almost linearly with increasing $\Delta\alpha$ in the blends .

4. Conclusion

Thermal diffusivity in a binary mixture of poly(phenylene oxide) and polystyrene was investigated by the AC Joule heating technique. A single T_g was observed in the temperature variation of thermal diffusivity at each blend ratio. T_g and the thermal diffusivity increased with increasing the weight fraction of PPO. The change rule of the thermal diffusivity at 50°C in the blend was almost described by the additivity of the thermal diffusivity in each polymer corresponding to the blend ratio. It was confirmed that the thermal diffusivity is related to the entanglement density in the blends. An almost linear relationship between $\Delta\alpha$ and T_g in the blends was also found.

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